ANALYSIS OF WASTEWATERS FOLLOWING U.S. EPA 200.7 USING THE AVIO 500 ICP-OES

The prevention and control of water pollution is of critical importance to protecting both human and environmental health. As a result, water must be monitored for pollutants at various stages, starting from the discharge of wastes and wastewaters all the way through the production of drinking water. Various techniques and methods are used depending on the pollutant and the type of water being analysed.

The U.S. Environmental Protection Agency (EPA) developed Method 200.7 for the determination of metals and trace elements in waters and wastes by ICP-OES, with the current version being Revision 4.4.1 While the scope of this method allows it to be applied to a variety of sample types, a common application is wastewater analysis.

This work focuses on the analysis of wastewaters following the guidelines provided in U.S. EPA Method 200.7.

Experimental

Samples and Sample Preparation

Four wastewater reference materials were used for method development and evaluation: Wastewater Low Levels and Wastewater High Levels (Inorganic Ventures™, Christiansburg, Virginia, USA) and Wastewater C and D (High Purity Standards™, Charleston, South Carolina, USA). These samples were prepared according to the instructions provided and analysed without further dilution. All measurements were made against external calibration curves prepared in 2% nitric acid (v/v) at the concentrations shown in Table 1. Yttrium (Y) and scandium (Sc) were added on-line to all blanks, standards, and samples as internal standards.

Instrument Conditions

All analyses were performed on the PerkinElmer Avio® 500 ICP Optical Emission Spectrometer (ICP-OES), using the conditions and parameters shown in Table 2. The analytical wavelengths and view modes are listed in Table 3. Despite the heavy wastewater matrix, the standard sample introduction components and conditions were used, including a total argon flow of 9 L/min.

Results and Discussion

Method 200.7 requires a variety of criteria to be satisfied which deal both with sample handling/preparation and the instrumentation. The following criteria relate specifically to the instrumentation and will be discussed in this work: linear dynamic range, quality control parameters, method detection limits (MDLs), instrument performance checks (IPC), spectral interference checks (SIC), accuracy, and stability.

Table 1. Calibration Standards.

Element	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)
Ag, Al, As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn	0.5	1	5
Na, Mg, K, Ca	20.5	51	105

Table 2: Avio 500 ICP-OES Instrumental Parameters.

Parameter	Value
Nebulizer	MEINHARD® Type K
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.70 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Integration Range	1-10 sec
Sample Uptake Tubing	Black/Black (0.76 mm id)
Internal Standard Tubing	Green/Orange (0.38 mm id)
Drain Tubing	Red/Red (1.14 mm id)
Replicates	4

Linear Dynamic Range

The linear dynamic range is defined as the highest concentrations which recover within 10% of their true values when analysed against the calibration curve used for analysis. Table 4 shows the determined linear dynamic ranges. For most elements, the linear range represents the highest concentration analysed, as determined by the highest typical sample concentrations for this application, not the linear range capability of the instrument.

Therefore, the linear dynamic range of the Avio 500 exceeds the requirements for this application. For higher-concentration samples, the linear range can be extended in a number of different ways: selection of less sensitive wavelengths, viewing in a different mode (i.e. axial/radial), varying the torch position, using a less-sensitive sample introduction system, and/or changing the viewing height in the plasma.

Initial QC: Initial Performance Check and Quality Control Sample

To check the quality of the calibration curve, two initial QC samples must be analysed directly after the calibration standards: an initial performance check (IPC) and quality control sample (QCS). The IPC should be made from the same stock standards used for the calibration standards, while the QCS must be made from second-source standards; both must recover within + 5% of their true values. For this evaluation, all elements were spiked at 1 ppm, with the exception of the minerals (Na, Mg, K, Ca), which were spiked at 50 ppm. As shown in Figure 1, both the IPC and QCS meet this criterion for all elements.

Method Detection Limits

According to Method 200.7, MDLs are determined by performing seven measurements of a blank which has been spiked at concentrations of two-three times the instrumental detection limits. The standard deviation of the seven measurements is then multiplied by 3.14 to attain the 99% confidence level. The MDLs are shown in Figure 2, along with the lowest certified values in the wastewater reference material analysed (Note: not all elements are certified in this reference material). The MDLs are significantly lower than the certified values, demonstrating the ability to easily measure low-level elements in wastewaters.

Spectral Interference Check

To determine if interelement correction equations (IECs) are required, a spectral interference check standard (SIC) containing 300 mg/L Fe and 200 mg/L Al was analysed. No significant interferences were found. The excellent spectral resolution of the Avio 500 optics eliminated the need for IECs. However, if samples are analysed which

Table 3: Elements, Wavelengths, and Plasma View Modes.

Element	Wavelength (nm)	Plasma View
Ag	328.068	Radial
Al	394.401	Radial
As	188.979	Axial
B	249.677	Axial
Ba	493.408	Radial
Be	313.107	Axial
Ca	315.887	Radial
Cd	214.440	Axial
Co	228.616	Axial
Cr	267.716	Axial
Cu	324.752	Axial
Fe	238.204	Radial
K	766.490	Radial
Li	670.784	Radial
Mg	285.213	Radial
Mn	257.610	Axial
Mo	203.845	Axial
Na	589.592	Radial
Ni	231.604	Axial
P	178.221	Axial
Pb	220.353	Axial
Sb	206.836	Axial
Se	196.026	Axial
Si	251.611	Axial
Sn	189.927	Axial
Sr	421.552	Radial
Ti	334.940	Axial
Tl	190.801	Axial
V	292.402	Axial
Zn	206.200	Axial
Sc (int std)	361.383	Radial
Y (int std)	371.029	Axial

Table 4: Linear Dynamic Range Pilot.

Elements	Linear Range (mg/L)
Al, Be, Mn, Ti	50
Ag, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li Mo, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Tl, V, Zn	100*
Mg	200
Ca, K, Na	500*

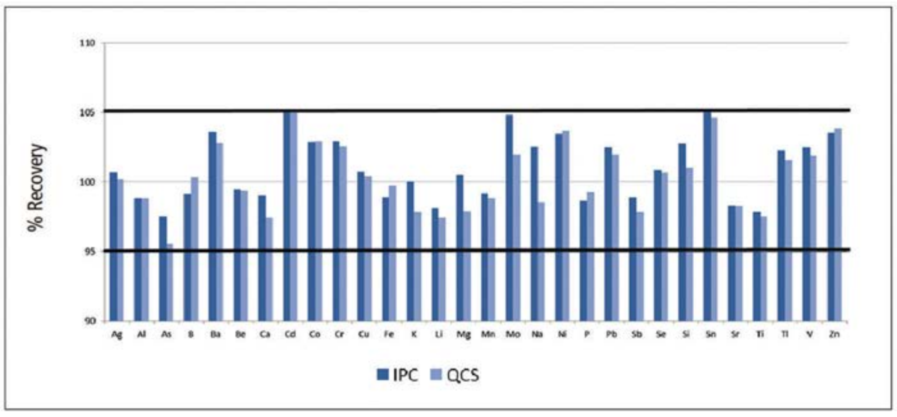

Figure 1: Recoveries for the IPC (dark blue) and QCS (light blue).

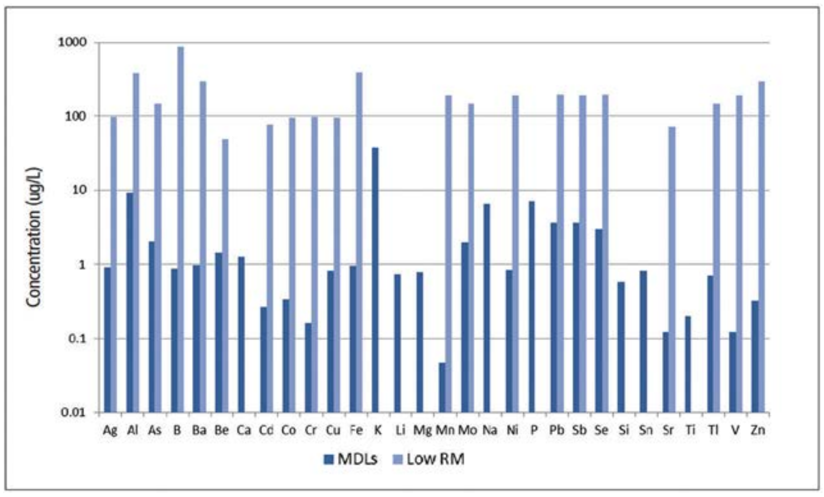

Figure 2: MDLs (dark blue) and certified values for low-level wastewater reference material (light blue). Not all elements in Method 200.7 are certified in the reference material.

Table 5: Certified Values in Wastewater Reference Materials (all units in mg/L).

Element	Wastewater Low	Wastewater High	Wastewater C	Wastewater D
Ag	0.098	0.927	0.15	0.25
Al	0.384	3.95	0.5	1
As	0.147	0.824	0.15	0.25
B	0.864	1.87	0.5	1
Ba	0.294	2.37	0.5	1
Be	0.048	0.832	0.15	0.25
Cd	0.078	0.927	0.15	0.25
Co	0.096	0.936	0.5	1
Cr	0.098	0.927	0.5	1
Cu	0.096	0.936	0.5	1
Fe	0.392	3.91	0.5	1
Mn	0.192	3.95	0.5	1
Mo	0.147	0.515	0.5	1
Ni	0.192	2.91	0.5	1
Pb	0.196	2.88	0.5	1
Sb	0.192	0.832	0.15	0.25
Se	0.196	1.85	0.15	0.25
Sr	0.072	0.468	0.5	1
Tl	0.147	0.824	0.15	0.25
V	0.192	1.87	0.5	1
Zn	0.294	1.85	0.5	1

contain high concentrations of other potential interferents, an IEC table can easily be created and implemented directly within Syngistix™ for ICP software.

Accuracy

To determine the accuracy of the method, four reference materials were analysed.

Table 5 shows the certified values for each of the reference materials, with the recoveries being plotted in Figure 3.

All recoveries are within 10% of the certified values, demonstrating the accuracy of the methodology. It should be noted that not all elements listed in Method 200.7 are certified in the reference materials.

To assess the ability to accurately measure the elements in Method 200.7 which are not present in the reference materials, spikes of the non-certified elements were added to the wastewater reference materials and analysed. Two different spike levels of each element were added to different reference materials, as shown in

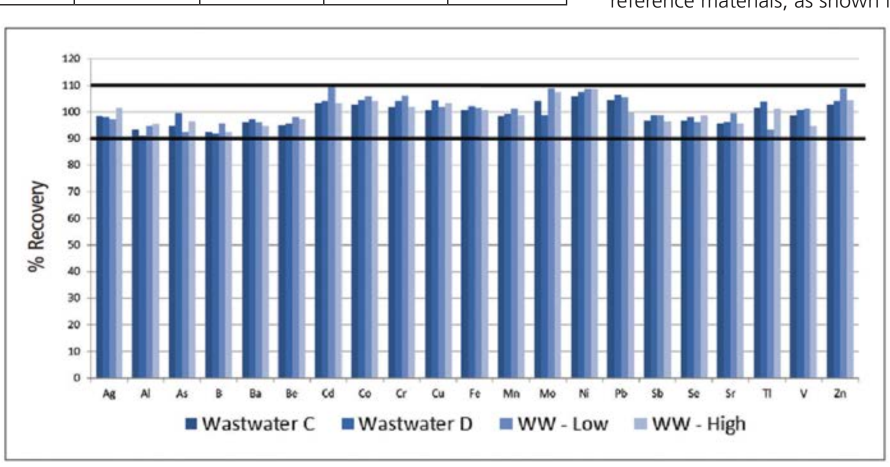

Figure 3: Recoveries in wastewater reference materials.

Table 6: Spike Levels of Non-Certified Elements.

Element	Spike (mg/L)	Reference Material to which Spike was Added
Li, P, Si, Sn, Ti	0.6	Wastewater C, Wastewater Low
	1.2	Wastewater D, Wastewater High
Ca, K, Mg, Na	75	Wastewater C, Wastewater Low
	150	Wastewater D, Wastewater High

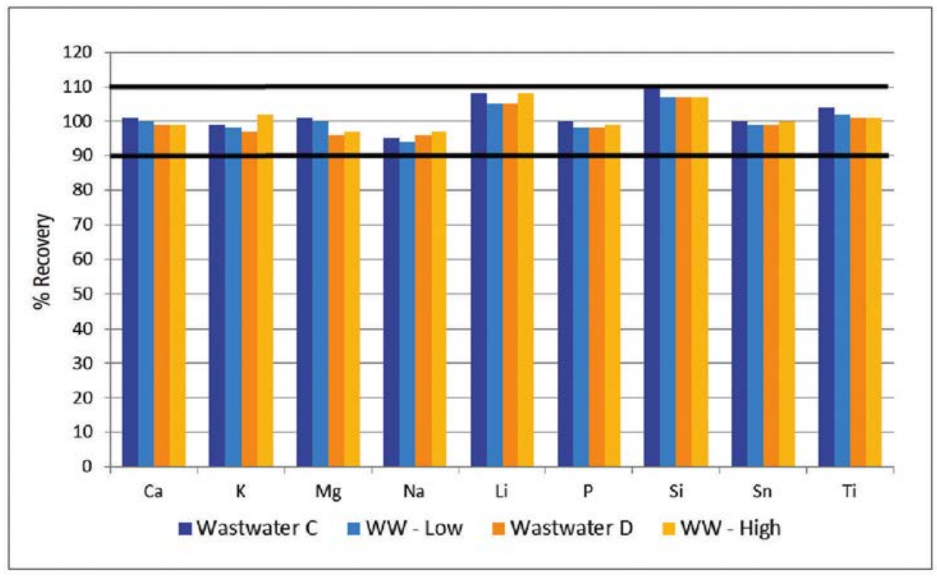

Figure 4: Spike recoveries of both lower (shades of blue) and higher (shades of orange) concentrations added to the wastewater reference materials.

Table 6, and the recoveries are plotted in Figure 4. All recoveries are within 10% of true values, further demonstrating the robustness of the methodology.

Stability

With the accuracy of the methodology established, the stability was assessed by analysing wastewater samples over 10 hours, with a QC check (the IPC) being analysed every ten samples. The plot in Figure 5 shows the stability, with all QC recoveries falling within 10% of their true value. In addition, the internal standard stability was monitored over the same analysis to determine overall instrumental drift. As shown in Figure 6, the internal standards varied by less than 7%, demonstrating the exceptional stability of the system. Instrumental design considerations, including the vertical torch and Flat Plate™ Plasma Technology, result in excellent stability, while taking advantage of the dual view capability and continuously switching between axial and radial plasma viewing modes for each sample.

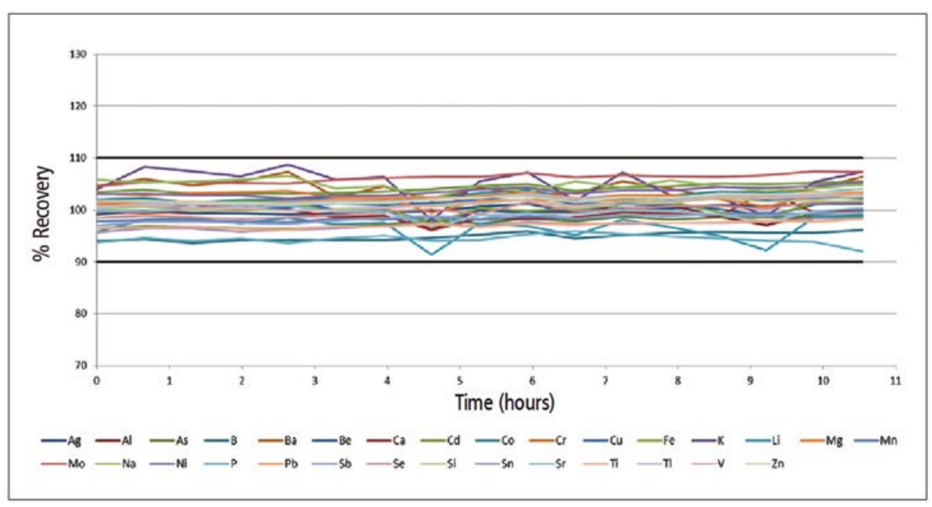

Figure 5: IPC recoveries during a 10-hour wastewater analysis.

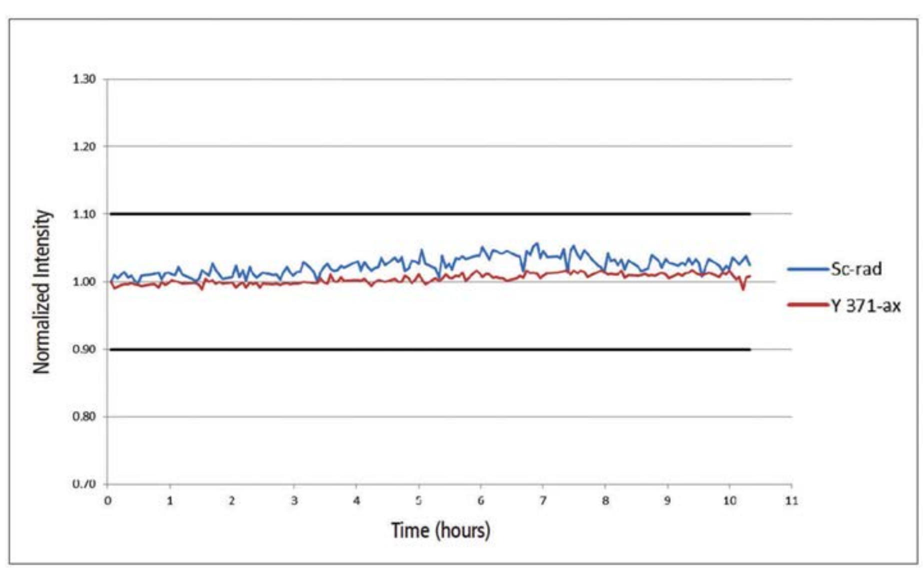

Figure 6: Internal standard recoveries in wastewater samples during a 10-hour analysis.

Conclusions

This work demonstrates the ability of the Avio 500 ICP-OES to analyse wastewater following the guidelines provided in U.S. EPA Method 200.7. With accuracy, reliability, robustness, and stability demonstrated through the analysis of reference materials and QC checks, the Avio 500 ICP-OES provides a robust solution for wastewater analysis, all while using a total argon flow of 9 L/min.This low argon consumption of the Avio 500 ICP-OES provides a faster return on investment for all laboratories.

Reference

1. Method 200.7, Revision 4.4: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry", United States Environmental Protection Agency, 1994.

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Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043 (flared) 09908587 (non-flared)
Drain Tubing, Red/Red (1.14 mm id), PVC	09908585
Internal Standard Tubing, Orange/Green (0.38 mm id), PVC	N0773111 (flared)
Instrument Calibration Standard 1:5000 mg/L Ca, K, Mg, Na	N9300218 (125 mL)
Instrument Calibration Standard 2: 100 mg/L Ag, As, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl V, Zn	N9301721 (125 mL)
Boron Standard, 1000 mg/L	N9300016 (125 mL) N9303760 (500 mL)
Cerium Standard, 1000 mg/L	N9303765 (125 mL) N9300110 (500 mL)
Lithium Standard, 1000 mg/L	N9303781 (125 mL) N9300129 (500 mL)
Cadmium Standard, 1000 mg/L	N9300176 (125 mL) N9300107 (500 mL)
Phosphorus Standard, 1000 mg/L	N9303788 (125 mL) N9300139 (500 mL)
Silicon Standard, 1000 mg/L	N9303799 (125 mL) N9300150 (500 mL)
Scandium Standard, 1000 mg/L	N9303798 (125 mL) N9300148 (500 mL)
Yttrium Standard, 1000 mg/L	N9303810 (125 mL) N9300167 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)